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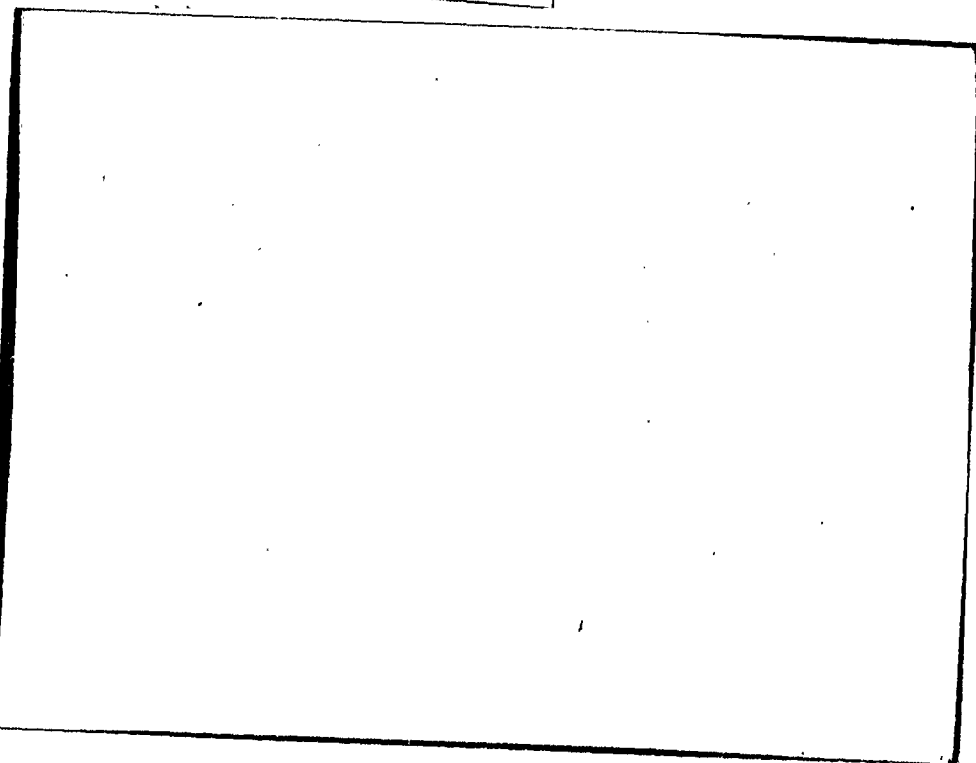
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**PARAMAGNETIC RESONANCE SPECTRA OF RARE EARTH IONS
IN THE CRYSTAL FIELD OF CALCIUM FLUORIDE ²**

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Technical Note No. 18

January 1962


Contract No. AF 61(052)-59


**Presented at the International Conference on Magnetism and Crystallography,
Kyoto, Japan, in September, 1961.**

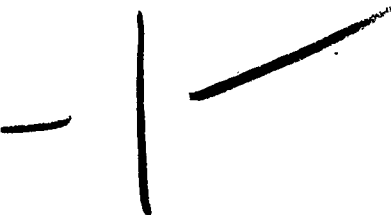
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**The research in this document has been sponsored in part by the Air Force
Office of Scientific Research, U.S.A.F., through its European Office of
Aerospace Research.**

ABSTRACT


Paramagnetic resonance data of various rare earth ions
in the crystal field of ^{Calcium Fluoride} ~~CaF₂~~, presented. It is found
that there are at least three types of symmetries, cubic,
axial and trigonal. ^{Some} ~~In particular the~~ spectra of ~~Co³⁺, V³⁺~~,
~~Fe³⁺, Mn³⁺~~ are presented.


—
* CERIUM (3+), YTTERBIUM (3+), ERBIUM (3+), AND NEODYMIUM (3+)



We have studied the paramagnetic resonance spectra of rare earth ions in the crystal field of calcium fluoride. These spectra can be classified as belonging to three types: a. spectra which indicate that the rare earth ions are exposed to a cubic field; b. spectra in which the anisotropic behaviour suggests an axial crystal field along the cubic directions; c. spectra in which the axial distortion is along the body diagonals of the cube.

The calcium ion with fluorite structure is surrounded by a cube of eight nearest fluorine ions. The trivalent rare earth ions substitute for the calcium ion. However, a charge compensation has to take place to preserve the neutrality of the crystal. From measurements of the X-ray lattice constants¹ and of the ionic conductivity² it has been shown that in well annealed crystals the main disorder introduced into the crystal by the addition of the rare earth ion is the formation of F^- interstitial (see Fig. 1). The empty sites which are available for the interstitial F^- ion are located at the center of the adjacent cube along one of the cubic axes. Supporting evidence for the F^- interstitial formation is found in the work of Bleaney et al.³

With proper thermal treatment, part or a large fraction of the interstitial fluorine ions can be removed from the adjacent cube next to the rare earth ion.⁴ In this case, the point symmetry of the rare earth ions approximates O_h . In some crystals, however, the predominant axial distortion is found from paramagnetic resonance spectra to be along the body diagonals of the cube. The optical spectra shows a number of strong bands and very poor ultraviolet transmission. It is likely that one of the fluorine ions at the corner of the cube is replaced by O^{2-} or OH^- ion. Supporting evidence is found that on heating the crystal in air this spectrum increases in intensity.

The respective crystal fields are given by

$$a) V_{\text{cubic}} = B_4^0 \left[O_4^0 + 5(O_4^4 + O_4^{-4}) \right] + B_6^0 \left[O_6^0 - 21(O_6^4 + O_6^{-4}) \right]$$

$$b) V_{\text{axial}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 (O_4^4 + O_4^{-4}) + B_6^4 (O_6^4 + O_6^{-4})$$

$$c) V_{\text{diagonal}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^3 (O_4^3 + O_4^{-3}) + B_6^3 (O_6^3 + O_6^{-3})$$

where B_n^m are crystal field coefficients proportional to $\frac{r^n}{R^{n+1}}$ and O_n^m are

operators transforming the corresponding spherical Legendre polynomials. The magnetic properties of these three types of spectra are very different and we shall illustrate this in a few selected examples. A full report of the magnetic properties of the rare earth ions in calcium fluoride will appear elsewhere.

$$\text{Er}^{3+} : 4H_{15/2}$$

a) In the cubic field of calcium fluoride, the 16-fold degeneracy splits into 3 quarters (Γ_8) and two doublets. The lowest levels are given by

$$-258.86 c - 162 d, \Gamma_8$$

$$-26 c - 312 d, \Gamma_7$$

where c and d are parameters signifying the fourth and sixth order contribution. For a point charge model they are given by

$$c = \frac{2^3}{3^3 \cdot 11.13} \frac{Z_0^2}{R^5} \quad d = \frac{2^4}{3^3} \frac{10}{11.13^2} \frac{Z_0^2}{R^7}$$

The observed g factor is 6.785 ± 0.002 . This is consistent with a Γ_7 ground state which gives g calculated = 6.79. A lowest Γ_7 level indicates that the rare earth spectrum is dominated to a large extent by the sixth order term in the potential.

b) An axial spectrum has been observed by Baker et al⁶ and by the author with $g_{\parallel} = 7.76$ and $g_{\perp} = 6.253$. This is consistent with the same doublet level except now exposed to an axial field since $\frac{g_{\parallel} + 2g_{\perp}}{3} \sim g$ cubic

c) A set of three lines, arising from the three inequivalent sites with axial symmetry along the three body diagonal directions, is observed in some crystals.⁷ Each ion can be described by g factors

$$g_{\parallel} = 2.23, \quad g_{\perp} = 8.9 \text{ and again } \frac{g_{\parallel} + 2g_{\perp}}{3} \sim g \text{ cubic.}$$

The g factors can be explained to arise from a doublet with

$$a | \pm 13/2 \rangle + b | \pm 7/2 \rangle + c | \pm 1/2 \rangle + d | \mp 5/2 \rangle + e | \mp 11/2 \rangle$$

with the coefficients b and d larger than a , c or e .

$$\text{Yb}^{3+} : {}^2F_{7/2}$$

(a) The cubic field suggests that Γ_7 is the ground state level. The wave function of the doublet is given by

$$\sqrt{\frac{3}{4}} | \pm 5/2 \rangle - \sqrt{\frac{1}{4}} | \mp 3/2 \rangle$$

and the calculated g factor = $24/7$. The observed g factor of 3.426 ± 0.001 is in essential agreement.⁸

(c) The spectrum along the body diagonals can be represented by the spin Hamiltonian

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta [H_x S_x + H_y S_y] + A S_z I_z + B(S_x I_x + S_y I_y) + P(I_z^2 - 1/3 I(I+1))$$

with $S = \frac{1}{2}$ and $I = \frac{1}{2}$ or $I = 5/2$.

The observed g factor is $g_{\parallel} = 1.323 \pm 0.001$ and $g_{\perp} = 4.387 \pm 0.002$ showing that this is the Γ_7 anisotropic level. This Kramer's doublet can be approximated with

$$0.940 | \pm 1/2 \rangle + 0.264 | \pm 7/2 \rangle + 0.209 | \mp 5/2 \rangle$$

The hyperfine part is expressed as

$$A^{171} = 354.6$$

$$B^{171} = 1168$$

$$A^{173} = 96$$

$$B^{173} = 320$$

$$P = 85 \pm 3. \quad \frac{g_n}{g_J} \frac{B}{A} \sim 1$$

all in 10^{-4} cm. These results indicate a large quadrupole moment of about 2.4 barns.

$$Nd^{3+} \quad 4I_{9/2}$$

(a) Calculations show that the ground state for all ratios of the fourth to sixth order parameters is given by a quartet $\sqrt{8}$. The wave functions and g factors are given by

<u>g value</u>	<u>transition</u>	<u>relative intensity</u>
2.24	$0.8722 -5/2\rangle - 0.4892 +3/2\rangle \rightarrow 0.8722 +5/2\rangle - 0.4892 -3/2\rangle$	20
1.15	$0.8722 +5/2\rangle - 0.4892 +3/2\rangle \rightarrow 0.05410 +9/2\rangle - 0.2981 +1/2\rangle + 0.9530 +7/2\rangle$	4.4
4.54	$0.5410 +9/2\rangle - 0.2981 +1/2\rangle + 0.9530 -7/2\rangle - 0.05410 -9/2\rangle - 0.2981 -1/2\rangle + 0.9530 +7/2\rangle$	0.075

The spin Hamiltonian of the $\sqrt{8}$ level in a cubic field is outlined by Bleaney⁹ applies here. The spectrum has been investigated and corresponds approximately to this Hamiltonian.

$$H = gB(H_i S_i) + fB(H_i S_i^3) \quad i = x, y, z.$$

The observed and calculated g factors are given in Table I¹⁰.

(b) The axial field spectrum has been investigated by Bleaney et al³ and remeasured by us¹⁰. The g factors are given $g_n = 4.412$ and $g_J = 1.301$. The ground state can be described possibly by

$$= a|+9/2\rangle + b|+1/2\rangle + c|+7/2\rangle$$

(c) A weak spectrum is also observed with the axial field along the body diagonals.

We have, in addition, observed the cubic field spectrum of Ce^{3+} , Dy^{3+} and Gd^{3+} , the axial field spectra of these ions. The axial spectra of ions with even number of electrons such as Tb^{3+} , and Tm^{3+} has been observed as well.⁷

A large part of this work has been performed in collaboration with Mr. M. Dvir, U. Rosenberger and Dr. G. Vincow.

TABLE I

Measured and calculated g factor of Γ_8 ground state of Nd^{3+} .

Direction	g exp.	g calc.
100	2.26	2.24
	1.10	1.15
110	1.45	1.46
	1.6	1.7

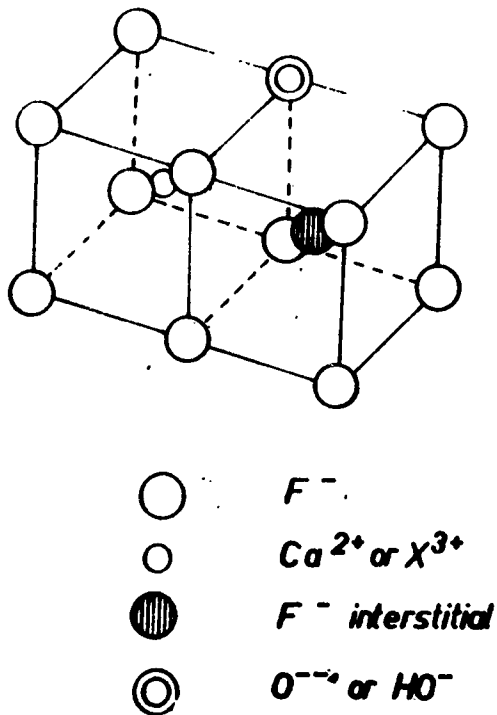
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Fig. 1.

Crystal Structure of CaF_2

The figure indicates the possible defect sites near the rare earth ion substituting for the calcium ion.



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DEPARTMENT OF PHYSICS
TECHNICAL REPORT NO. 18
JANUARY 1962

AF 61(052)-59
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